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Production of foam sheets

The invention relates to a process for producing foam sheets with a density of from 20 to 200 $g \cdot l^{-1}$ and with a cross section of at least 50 cm^2 based on styrene polymers which comprise graphite particles to reduce thermal conductivity.

Extruded polystyrene foams (XPS) are widely used to insulate buildings and parts of buildings. For this application the foam sheets have to have very low thermal conductivity. Nowadays, halogen-free blowing agents, preferably CO_2-containing blowing agent mixtures, are used for producing XPS sheets in order to protect the environment. However, CO_2 diffuses out of the foam cells significantly more rapidly than fluorine-containing gases and is replaced by air. The thermal conductivity of XPS sheets produced with CO_2-containing blowing agents is therefore somewhat higher than that of XPS sheets produced with fluorohydrocarbons. It is known from EP-A 863 175 that adding graphite particles can reduce thermal conductivity during XPS production. However, it has been found that the nucleating action of the graphite here gives a very fine-celled foam, meaning that it is not possible to produce thick sheets. It is an object of the present invention, therefore, to provide very thick XPS sheets with low thermal conductivity.

We have found that this object is achieved if, during the production of foam sheets with a density of from 20 to 200 $g \cdot l^{-1}$ and with a cross section of at least 50 cm^3 by extrusion and foaming of a mixture made from a styrene polymer, from 3 to 15% by weight of a volatile blowing agent and from 0.2 to 10% by weight of graphite particles, based in each case on the styrene polymer, if desired with conventional additives, the blowing agent used comprises a mixture made of
from 95 to 30% by weight of CO_2,
from 5 to 70% by weight of H_2O, and
from 0 to 60% by weight of a volatile organic compound.

WO 93/25 608 describes the production of XPS foams with a bimodal foam structure, using a blowing agent mixture made from CO_2, H_2O and C_2H_5OH, with addition of carbon black during extrusion. The water content in the blowing agent mixture is said to be responsible for the bimodal foam structure, and the carbon black additive is intended to reduce thermal conductivity. However, it has been found that a bimodal foam structure is disadvantageous since it makes operations on the foam sheets, e.g. sawing, milling, cutting or embossing, more difficult. Surprisingly, it

has been found that adding graphite instead of carbon black not only further lowers the thermal conductivity but also can prevent the formation of a bimodal foam structure. WO 93/25 608 also gives no indication that the water content in the blowing agent mixture permits thick sheets to be produced.

WO 94/09 975 teaches that XPS foams with a monomodal foam structure are obtained when a CO_2/H_2O blowing agent mixture is used if the water-solubility of the polymer melt is increased. No mention is made in this publication of adding graphite particles in the production of XPS.

For the purposes of this invention, styrene polymers are polystyrene and copolymers of styrene in which there is at least 50% by weight of copolymerized styrene. Examples of possible comonomers are α-methylstyrene, ring-halogenated styrenes, ring-alkylated styrenes, acrylonitrile, (meth)acrylates of alcohols having from 1 to 8 carbon atoms, N-vinyl compounds, such as vinylcarbazole, maleic anhydride or else small amounts of compounds which contain two polymerizable double bonds, such as butadiene, divinylbenzene or butanediol diacrylate.

The foam sheets comprise from 0.2 to 10% by weight of graphite particles uniformly distributed, preferably from 1 to 8% by weight of graphite with a particle size of from 1 to 100 µm, preferably from 2 to 20 µm.

It is advantageous to use flame retardants in producing the XPS, preferably from 0.5 to 5% by weight of organic bromine compounds with a bromine content of more than 70%, e.g. hexabromocyclododecane, preferably together with from 0.1 to 0.5% by weight of an organic compound which has labile C-C bonding or labile O-O bonding, for example dicumyl peroxide or preferably dicumyl.

Other conventional additives and/or auxiliaries which may be added to the polystyrene matrix are antistats, stabilizers, dyes, fillers and/or nucleating agents, in the usual amounts.

The blowing agents used comprise from 3 to 15% by weight, preferably from 4 to 12% by weight, based on the styrene polymer, of a mixture made of
from 95 to 30% by weight, preferably from 90 to 40% by weight, of CO_2,
from 5 to 70% by weight, preferably from 10 to 60% by weight, of H_2O, and

from 0 to 60% by weight, preferably from 0 to 30% by weight, of a volatile organic compound.

The volatile organic compound preferably has a boiling point of from 0 to 100°C, in particular from 30 to 80°C. Examples of suitable compounds are alcohols, aliphatic hydrocarbons, ketones and ethers. Ethanol is particularly preferred.

An advantage of adding water to the blowing agent mixture is that the amount of combustible organic blowing agents can be reduced or even dispensed with entirely. When graphite is used instead of carbon black as an agent for reducing the thermal conductivity of the foam sheets, then even when H_2O is used as blowing agent a monomodal foam structure is obtained. It appears that the concomitant use of water as blowing agent reduces the nucleating effect of the graphite, so that it is also possible to produce thick foam sheets.

The percentages mentioned in the examples are based on weight.

Examples

The foam samples are extruded on a tandem plant. This is composed of a twin-screw ZSK53 extruder and a single-screw cooling extruder (KE 90). Polymer and additives were introduced to the twin-screw extruder. The polymer was melted at 210°C and the mixture of the blowing agents was injected in its entirety at a single point. The melt comprising blowing agents was then cooled in the second extruder to 120-135°C, the temperature needed for foaming. The throughput was 50 kg/h, and the die had a width of 70 mm. The height of the die gap was 3 mm. Graphite powder (AF spez. 96-97, average particle size 6 µm, from Graphitwerk Kropfmühle) was added to the polystyrene. The makeup of the blowing agent and the results are shown in the table.

Table

Example	Blowing agent mixture %			Additives %			Density	Thickness	Th. cond. λ
	CO_2	H_2O	C_2H_5OH	Graphite	Carbon black	Talc	$g \cdot l^{-1}$	mm	$mW \cdot m^{-1} \cdot K^{-1}$
1	2	3	-	-	-	2	42	66	38
2	2	3	-	-	2	-	43	67	35
3	2	3	-	2	-	-	46	72	32
4	2	2	1	2	-	-	44	70	32
5	2	-	3	2	-	-	56	48	33

Examples 3 and 4 are according to the invention

The foam in Example 2 has a bimodal foam structure.